Dan Johansson

Carbohydrate degradation and dissolution during Kraft cooking

Modelling of kinetic results

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Till minne av
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Abstract

Chemical pulp fibres from wood are commonly used in products associated with packaging as well as with printing and writing. The prevalent way of liberating fibres is by subjecting wood chips to Kraft cooking. This process has a history of almost 130 years and should be both well described and well established. However, new products and new applications that use fibres as an important renewable resource make it all the more important that the properties of fibres be controllable. The properties of wood fibres are influenced by their carbohydrate composition which, in turn, is dependent on the cooking conditions used. This thesis studies the degradation and dissolution of the different carbohydrates during Kraft cooking and summarizes the results in kinetic expressions.

Industrial wood chips from Norway spruce (Picea abies) were cooked at a high liquor-to-wood ratio (50:1) in an autoclave digester at varying concentrations of hydroxide ions, hydrogen sulphide ions and sodium ions as well as varying temperatures. The pulps were analysed for carbohydrate composition, kappa number, content of hexenuronic acid and pure cellulose viscosity, where the cellulose content in the pulp sample was used for calculating the viscosity. Kraft cooking of Eucalyptus urophylla and Eucalyptus grandis was also studied, using industrial liquor-to-wood ratio (4:1), to examine the relationship between hexenuronic acids and the amount of xylan in the pulp samples.

For Kraft cooking of Norway spruce it was found that an increase in the concentration of hydroxide ions increased the rate of dissolution of the carbohydrates and the degradation of the cellulose degree of polymerization (DP). However, measured at a kappa number of 30, it was also found that a low hydroxide ion concentration could lower the carbohydrate yield and the pure cellulose viscosity dramatically. The hydroxide ion concentration not only affected the rate of dissolution but also the amount of xylan that reacted in the slower, final phase. Both cellulose and hemicelluloses were found to be affected by the hydrogen sulphide ion concentration. The dissolution of cellulose and hemicelluloses at varying sodium ion concentrations was found
to be affected in different directions. The effect of sodium ion concentration on the DP was found to be dependent on the method of evaluation. The pulp viscosity was found to be affected twice as much by the sodium ion concentration than the pure cellulose viscosity. For Kraft cooking of hardwood it was found that a high xylan yield not always was synonymous with a high hexenuronic acids content.
Sammanfattning

Vedfibrer är mycket vanliga i flera förpackningsapplikationer så väl som i tryck och skrivpapper och det vanligaste sättet att frigöra fibrerna från varandra är genom sulfatkokning av vedflis. En process med en 130 årig historia borde kanske vara väl så noggrant genomgången och beskriven. Dock kräver nya produkter och nya applikationer med fibrer en ökad möjlighet att påverka fibregenskaperna. Fibernas egenskaper påverkas av den kemiska sammansättningen vilken i sin tur beror av betingelserna i sulfatkoket. Denna avhandling studerar nedbrytningen och utlösningen av de olika kolhydraterna under sulfatkoket och sammanfattar resultaten i kinetikuttryck.


natriumjoner var dubbelt så stor på massaviskositeten jämfört med den rena cellulosaviskositeten. Vid sulfatkokning av lövved visade sig att en hög xylanhalt inte direkt innebar en hög halt hexenuronsyra.
List of Papers

This thesis is a summary of the following papers. They are appended at the end of the thesis and reprinted with the kind permission of the publishers.


# Table of Contents

1 Objectives of this study

2 Introduction

2.1 The structure of wood

2.1.1 The chemical composition of wood

2.1.2 The morphology of wood

2.2 Kraft Cooking

2.2.1 Chemical aspects of the Kraft cooking process

2.2.2 Processing aspects of the Kraft cooking process

2.3 Carbohydrate degradation and dissolution kinetics in softwood Kraft cooking

2.4 Carbohydrate degradation and dissolution kinetics in hardwood Kraft cooking

3 Experimental

4 Results and Discussion

4.1 Carbohydrate degradation and dissolution in softwood Kraft cooking

4.1.1 The effect of temperature

4.1.2 The effect of the hydroxide ion concentration

4.1.3 The effect of the hydrogen sulphide ion concentration

4.1.4 The effect of sodium ion concentration

4.2 A kinetic model for carbohydrate degradation and dissolution

4.2.1 The kinetics of the dissolution of cellulose

4.2.2 The kinetics of the dissolution of xylan

4.2.3 The kinetics of the dissolution of glucomannan

4.2.4 The kinetics of the cellulose viscosity

4.2.5 The kinetics of the degradation of hexenuronic acid

4.3 The relationship between hexenuronic acids and xylan in eucalyptus Kraft pulp

5 Industrial aspects

5 Conclusions

6 Acknowledgements

7 References
1 Objectives of this study

The pulp and paper industry is currently struggling with higher energy costs, stronger competition and thereby also higher raw material prices. It is of great interest today in the world, where a lot of attention is paid to the environment in general and global warming in particular, to further develop the production and quality of pulp to fit the needs of the future. One simple and ever-popular issue is the yield, where a better use of the raw material is of interest for both improved economics within the industry and less wastage of resources. An alternative is to use renewable pulp fibre in new applications previously based on non-renewable resources.

Controlling the properties of pulp in a more precise and accurate way could be vital in optimizing yields and to meet the requirements of new applications; for this to be possible, it must first be understood how pulp is produced that meets these demands. One of the objectives of this study has therefore been to elucidate how the different carbohydrates in pulp react to varying cooking conditions in the Kraft cooking process. For reasons of comparison, the data has been fitted to mathematical expressions describing the kinetics of the dissolution of the polymers. The expressions make it easy to compare the results and formulate chemical explanations.

A further objective has been to find a better way of describing the degradation of the cellulose polymer in the Kraft cook than with pulp viscosity normally used.

The formation and degradation of hexenuronic acids have also been objectives of this study in order to understand them better. Hexenuronic acids affect the quality of pulp, so the ways in which they can be controlled is of great importance.
2 Introduction

2.1 The structure of wood

Wood is built up of cells comprised of carbohydrates, lignin, and extractives. The most common cells are referred to as “fibres”, the chemical composition of which differs significantly not only between softwood and hardwood but also within the same genus. The cells are the structural elements of wood tissue; when they are grouped together to form e.g. a tree, they ensure that the organism is able to withstand the natural forces to which it is exposed.

2.1.1 The chemical composition of wood

*Cellulose*

The largest contributor to the characteristics of the wood cell is the carbohydrate cellulose, which constitutes around 50% of its total organic mass. Wood cellulose is a linear polymer and has a degree of polymerisation, DP, of up to 10,000 monomer \(\beta\)-glucose units coupled by \(\beta(1 \rightarrow 4)\)-glucosidic bonds, as seen in Figure 1 (Timell (1957)).

![Figure 1. The structure of cellulose.](image)

The cellulose polymers are linked together by hydrogen bonds between the hydroxyl groups on the cellulose backbone to form bundles known as “microfibrils”. These microfibrils exhibit a fairly crystalline structure.
Hemicelluloses

Carbohydrates with a DP much lower than that of cellulose, an average DP = 100–200 (Meier (1958), Croon and Enström (1962), Simonson (1963)), and arranged in a less ordered amorphous structure of branched polymers is often organized under the collective name “hemicelluloses”. The backbone of these carbohydrates is built up of different sugar monomers, with a selection of monomeric substituents along the sides.

Softwood hemicelluloses

The hemicelluloses in softwood add up to 25-30% of the dry matter. The two most important hemicelluloses are O-acetyl-galactoglucomannan, commonly denoted “glucomannan”, and arabino-(4-O-methyl-glucurono)xylan, simply known as “xylan” (Hamilton and Thompson (1958); Jacobs and Dahlman (2001)).

Glucomannan is the most common hemicellulose found in softwood and has a backbone of glucose and mannose monomers with galactose substituents. The monomers in the backbone are bound with a (1-4)-linkage and are partially O-acetylated on the C-2 and C-3 position (Figure 2). Glucomannan is divided into two fractions, depending on the monomer ratio. One fraction has a low ratio of galactose monomers whilst the other is rich in galactose units (Sjöström (1993)).

![Figure 2. The structure of O-acetyl-galactoglucomannan.](image-url)
Xylan consists of a (1-4)-linked backbone of xylose monomers (Figure 3). The xylose is also partially substituted at C-2 by 4-O-methylglucuronic acid that under alkaline conditions, e.g. in a Kraft cook, reacts to form hexenuronic acid. Arabinose monomers are also substituted on the xylose backbone.

Hardwood hemicelluloses

Hardwood also consists of two major hemicelluloses. In common with softwood, these are also normally referred to as “glucomannan” and “xylan” even though they differ in structure and the proportions in which they are present in the native wood. The total content of hemicellulose in hardwood varies between 15-30%.

The most common hemicellulose present in hardwood is xylan, or O-acetyl-(4-O-methyl-glucorono) xylan (Figure 4), which is the more accurate name. The backbone of this consists of (1-4)-linked xylose residues which are partially substituted in C-2 and C-3 with O-acetyl groups. The xylose monomers also have 4-O-methylglucuronic acid substituents along the polymer chain.
Glucomannan in hardwood is responsible for only a small percentage of the mass of the native wood. It consists of (1-4)-linked glucose and mannose monomers in the backbone and has partial O-acetyl substituents in the C-2 and C-3 positions (Figure 5).

![Figure 5. The structure of O-acetyl glucomannan.](image)

**Lignin**

The lignin polymer in wood, in contrast to the simple straight polymer structure of carbohydrates, is very complex and shows a 3D matrix-like arrangement. The polymer is built up of phenylpropane units with different substituents on the aromatic groups (Figure 6).

![Figure 6. The three most common lignin building blocks. From left to right: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.](image)

The proportion of the three alcohols in the lignin polymer varies between softwood and hardwood as well as between different species. Softwood lignin, which is about 25-30% of the dry mass of wood, contains almost
exclusively “guaiacyl lignin”, is composed of coniferyl alcohol units. Hardwood lignin, which is about 20-25% of the dry mass of wood, is composed of coniferyl and sinapyl alcohol and is often called “guaiacyl-syringyl lignin” (Sjöström (1993)).

Other components

In addition to the components presented earlier, wood also contains some pectic substances, which are a type of carbohydrate not unlike the hemicelluloses. They are, however, present to a much lesser extent.

Another group of substances natively inherent to wood is the “extractives”; as the name implies, all of the substances are extractable either with water or an organic solvent, such as acetone. The extractives comprise a few percent of the total dry mass of wood.

2.1.2 The morphology of wood

When a tree grows, new wood cells are formed. During the lifetime of a cell, its chemical composition is built up according to a specific schedule. However, when the cell dies, it takes on the appearance that we are familiar with as being a wood fibre and the chemical composition specific for the species. Moving inwards from the outside, the first layer in the wood cell is the primary wall (P), the first, second and third layers the secondary walls (S1, S2 and S3) and, finally, there is the lumen (L) (Figure 7). The fibres are arranged side by side in the tree, separated by the middle lamella (ML).
Figure 7. A schematic diagram of wood cells arrangement

Cellulose, hemicelluloses, lignin and the other components are ordered in varying composition in the different parts of the fibre wall depending on the species of the plant. There is still uncertainty as to the way in which all the components within the fibre wall are linked together, although it is well known that lignin is bonded chemically to the carbohydrates (Björkman (1956, Kosikova et al. (1979, Eriksson et al. (1980)). It has later been proposed by Lawoko (2005) that there are two types of lignin: one more associated with glucomannan and one more associated with xylan.

2.2 Kraft Cooking

The fibres in wood must be liberated from each other in order to produce pulp for paper and paperboard. This may be done using mechanical force or chemicals. The most widely-used method is to liberate the fibres by Kraft cooking, i.e. a chemically-based process that uses the active cooking chemicals hydroxide and hydrogen sulphide ions.

2.2.1 Chemical aspects of the Kraft cooking process

The aim of the Kraft cooking process is to degrade the lignin polymer, which acts as a kind of adhesive between the fibres, so that they can be separated from each other. This is done by the active hydroxide and hydrogen sulphide
ions present in the cooking liquor in combination with energy in the form of elevated temperatures. The drawback of the Kraft cooking process is that the residual lignin in the pulp makes it dark in colour: extensive bleaching is therefore necessary before fully-bleached pulp is obtained. Lignin is not the only wood component that degrades in the cooking process: cellulose and hemicellulose are also degraded and dissolved to some extent or other: This results in a low yield when compared to other pulping processes.

There are also other negative reactions regarding the carbohydrates that are not as important for the yield as they are for the quality of the pulp. One of the substituents on the xylan backbone in both softwood and hardwood, i.e. 4-O-methylglucuronic acid, reacts with the cooking chemicals with the formation of hexenuronic acid as a result, as can be seen in Figure 8. The hexenuronic acid reduces the brightness stability of the pulp and increases the consumption of bleaching chemicals.

![Chemical reactions diagram](attachment:image.png)

Figure 8. The formation of hexenuronic acid (1), the degradation of methylglucuronic acid (2) and the degradation of hexenuronic acid (3).

Chemical reactions apart, it is important to remember that a wood chip is a solid material and that the aspects of mass transfer into and out of the chip affect the Kraft cook significantly. The active cooking chemicals have to diffuse into the reaction site of the chip in the same way as the degraded parts of the lignin or carbohydrate have to be transported out in the free cooking liquor.
2.2.2 Processing aspects of the Kraft cooking process

The Kraft process was established in 1879 by Carl Dahl in Germany. At the beginning of the industrial era of Kraft cooking, the batch digester was loaded with wood chips, filled up with cooking chemicals and then heated to the cooking temperature. Chips and cooking liquor were blown out of the digester after being cooked; the resulting pulp was washed and a new batch was loaded. The Kraft pulping process has developed significantly over the years and there are now two principal types of processes available on the market. One is the batch process based on the initial cooking technique but with a much more energy efficient setup, whereby the spent cooking liquor is recycled and reused in another digester. The second is a continuous process based on one single digester in which the chips are fed into the top, the cooking liquor is recycled and the pulp is pumped out of the bottom.

The Kraft cooking process is currently based on the concept of modified Kraft pulping that was developed during the 1970s and 1980s at STFI and KTH in Stockholm, Sweden. Certain principles were established for the so-called “selective cook”. Firstly, the alkali concentration should be levelled out (Norden and Teder (1979), Teder and Olm (1981) and Sjöblom et al. (1983)), in direct contrast to the earlier technique where all the white liquor was charged at the beginning of the cook and resulted in a very high initial alkali concentration. Secondly, the concentration of hydrogen sulphide ions should be as high as possible, especially at the beginning of the bulk phase (Teder and Olm (1981) and Sjöblom et al. (1983)). The temperature should be low and, finally, the concentration of dissolved lignin and sodium ions should be as low as possible, especially in the final phase of the Kraft cook (Kubes et al. (1983), Teder and Olm (1981) and Sjöblom et al. (1983)). It has, however, since been shown that, in the initial phase of the cook, the dissolved lignin has a positive effect on delignification (Sjödahl (2004)).
2.3 Carbohydrate degradation and dissolution kinetics in softwood Kraft cooking

The reaction kinetics of carbohydrate degradation and dissolution have been studied in various ways over the years using model substances, wood meal or chips, as outlined below. The goal has been to increase understanding of the Kraft cook; the results can then be used to simulate the process to find ways of improving the quality and/or yield of the pulp.

Model substances have been used in order to isolate a specific reaction, or set of reactions, for one single component under well-defined conditions. The degradation of carbohydrates under alkaline conditions is often described by the steps: initiation, chain propagation at the reducing end-group followed by endwise degradation, peeling, of the polymer to the point when a stable end-group (known as a “chain termination”) is formed. The pattern could start all over again after an alkaline hydrolysis of the polymer chain, resulting in a new, reducing, end-group. Haas et al. (1967) studied the effects of alkaline on the propagation and termination of the cellulose chain in cotton cellulose. They found the activation energy for the propagation reaction to be 103 kJ/mol and 135 kJ/mol for the termination reaction. The peeling reaction was also studied for amylase: Lai and Sarkanen (1969) followed the peeling reaction on a soluble polymer in alkaline solution. Green et al. (1977) studied the endwise peeling reaction too, and found that it was seen not only at lower temperatures but also at ordinary pulping temperatures. Young and Liss (1978) compared the reactivity of different glucomannans for the endwise peeling reaction. They found the activation energy for the peeling reaction of spruce glucomannan to be 103 kJ/mol and that a higher hydroxide ion concentration leads to an increase in the termination reaction, resulting in a higher glucomannan yield.

Lai and Sarkanen (1967) studied the alkaline hydrolysis of cotton cellulose. They measured the viscosity of the cotton cellulose sample after the reaction and found the activation energy for alkaline hydrolysis to be 150 kJ/mol. Agarwal et al. (1992) refined the approach of fitting the data from Lai and Sarkanen (1967) into a kinetic expression, obtaining an activation energy of 142 kJ/mol for the chain scission caused by alkaline hydrolysis.
Wood meal is often preferred to cotton cellulose or model substances when simulating pulping conditions and minimizing the effect of diffusion. Kondo and Sarkanan (1984) used Western Hemlock wood meal to study the initial degradation of hemicelluloses in Kraft and soda cooking. They assumed that propagation and termination had similar activation energies, which they found to be 93 kJ/mol. The hydrogen sulphide ion concentration was found not to affect the degradation of hemicellulose.

Another study carried out on wood meal was that presented by Wigell et al. (2007) on *Pinus sylvestris*. They modelled the peeling, termination and alkaline hydrolysis of galactoglucomannan in soda cooking using the expressions found in Equations 1a-1c:

\[
\frac{dG_p}{dt} = k_p R(t)[OH^-] \quad \text{[1a]}
\]

\[
\frac{dR}{dt} = -k R(t)[OH^-] \quad \text{[1b]}
\]

\[
\frac{dG_h}{dt} = k_h G(t)[OH^-] \quad \text{[1c]}
\]

where \( G_p \) is glucomannan lost due to primary peeling, \( R \) the frequency of reducing end-groups, \( G_h \) the glucomannan lost due to alkaline hydrolysis and the following secondary peeling and \( k \) the rate constant. \( l, m \) and \( n \) are the exponents of the hydroxide ion concentration. Wigell et al. (2007) found, just as Kondo and Sarkanan (1984) had assumed earlier, that the activation energy was fairly similar for the peeling and stopping reactions, with values of 111 kJ/mol and 110 kJ/mol, respectively. The alkaline hydrolysis was found to have an activation energy of 89 kJ/mol which, surprisingly, is lower than the activation energy found for the peeling reaction. However, not many results in this study were from the latter part of the cook, where alkaline hydrolysis is to be found. Wigell et al. (2007) also found that the stopping reaction, compared to the peeling reaction, is favoured by a higher hydroxide ion concentration.
Experiments on wood chips are probably the most common way of studying pulping reactions. The focus is most often on the dissolution of the different components and/or the viscosity of the pulp, i.e. the degree of polymerization of the carbohydrates. The kinetic models developed in this area show varying complexity and different focuses. Some models study only the dissolution or degradation of the carbohydrates in the pulp whilst others focus on the consumption of cooking chemicals or diffusion of the cooking liquor into the chips. All of the models presented here, however, contain some aspect or other of carbohydrate degradation.

When Vroom (1957) developed the H-factor model he studied not only lignin degradation but also carbohydrate loss. This model was the simplest possible, with all carbohydrates expressed as one component dependent on temperature and time. It was not until Smith and Williams (1974) presented their work based on a continuous Kamyr digester that the carbohydrates were separated and modelled singly. These models were later reworked by Christensen et al. (1983) to predict results more accurately. The model presented by Christensen is shown in Equation 2:

$$\frac{dC}{dt} = \left[ k' OH^- + k'' OH^- \left( HS^- \right) \right] (C - C_0)$$  \hspace{1cm} [2]

The rate constant $k$ depends on temperature through an Arrhenius expression, $C$ is the component studied and $C_0$ is the unreactive part of the component. $a$ and $b$ are the exponents of the hydroxide ion and hydrogen sulphide ion concentration, respectively. Christensen fitted data published earlier into his equation, and found the activation energies for the cellulose, glucomannan and xylan loss of yield to be 42, 38 and 167 kJ/mol, respectively. The models presented by Smith and Williams (1974) and Christensen et al. (1983) belong to the model family usually known as the “Purdue Model”, named after the university where it was developed. Saltin (1992), Wisnewski et al. (1997) and Bhartiya and Doyle III (2002) are examples of other publications based on the same model.
The Purdue Model was also developed to work on two components of lignin. A model that covers both lignin and carbohydrate dissolution is the “Three Stage Model” developed at the University of Washington. Originally, the model predicted the content of carbohydrates in the pulp that was dependent on the lignin dissolution, as presented in Gustafson et al. (1983). All the carbohydrates were merged into one component and modelled in three consecutive phases, as shown in Equations 3a-3c.

\[
\frac{dC}{dt} = 2.53[OH^-]^{1.21} \frac{dL}{dt} \quad [3a]
\]

\[
\frac{dC}{dt} = 0.47 \frac{dL}{dt} \quad [3b]
\]

\[
\frac{dC}{dt} = 2.19 \frac{dL}{dt} \quad [3c]
\]

where \( C \) is the carbohydrate content and \( L \) the lignin content of the pulp. The lignin content is then based on three different kinetic expressions, one for each phase.

The Three Stage Model was later refined and a model was published by Pu et al. (1991). They divided the carbohydrates further into two parts, cellulose and hemicelluloses, which were not dependent on the lignin content of the pulp (Equations 4-5). The idea behind the Three Stage Model is that the cook is divided into three separate phases with different kinetic expressions explaining each part of the cook, i.e. there are very distinguished transitions between the phases of the cook.

Initial phase:

\[
\frac{dC}{dt} = -k_{C1} \left( \frac{C_0}{CA} \right) [OH^-]^{1/3} (C - Cr)
\]

\[
\frac{dH}{dt} = -k_{H1} \left( \frac{H_0}{HR} \right) [OH^-]^{1/3} (H - Hr)
\]

\[
\frac{dC}{dt} = 2.53[OH^-]^{1.21} \frac{dL}{dt} \quad [3a]
\]

\[
\frac{dC}{dt} = 0.47 \frac{dL}{dt} \quad [3b]
\]

\[
\frac{dC}{dt} = 2.19 \frac{dL}{dt} \quad [3c]
\]

where \( C \) is the carbohydrate content and \( L \) the lignin content of the pulp. The lignin content is then based on three different kinetic expressions, one for each phase.
Intermediate phase:

\[
\frac{dC}{dt} = -k_{c2} e^{-\frac{E}{RT}} \left[ \frac{[OH^-]}{[OH^-]} \right] (C - C_r)
\]  \hspace{1cm} \text{[5a]}

\[
\frac{dH}{dt} = -k_{H2} e^{-\frac{E}{RT}} \left[ \frac{[OH^-]}{[OH^-]} \right] (H - H_r)
\]  \hspace{1cm} \text{[5b]}

where \( C \) is cellulose, \( C_r \) an unreactive part of cellulose, \( H \) the hemicelluloses and \( H_r \) an unreactive part of the hemicelluloses. \( E \) is the activation energy, and was found to be extremely low for the initial phase for both cellulose and hemicelluloses. The activation energy for the dissolution of cellulose and hemicelluloses in the intermediate phase was found to be 150 and 93 kJ/mol, respectively.

Later on, Andersson et al. (2003) merged the ideas of the Purdue Model with those of the Three Stage Model, and presented a model that predicted the content of cellulose, glucomannan and xylan in the pulp through three parallel phases per component. The expression used for each carbohydrate component is given in Equation 6:

\[
\frac{dW_i}{dt} = -k_i \left( \frac{[OH^-]}{[OH^-]} \right)^a + k_2 W_i
\]  \hspace{1cm} \text{[6]}

where \( W \) is the wood component in question in the different phases, \( k_i \) the Arrhenius expression and \( k_2 \) a constant used to describe the dissolution of carbohydrates seen already at low alkali concentrations. Andersson et al. (2003) found the activation energies for all three carbohydrate components to be 50, 144 and 144 kJ/mol for the initial, intermediate and final phase, respectively. The activation energy used for the initial phase was based on the results obtained by Olm and Tistad (1979). The exponent for the alkali dependence \( a \) was found for all three carbohydrates to be 0.1, 1.0 and 1.0 for the initial, intermediate and final phases, respectively.
It is not only the carbohydrate yield loss that have been modelled but also the hexenuronic acid content. Hexenuronic acids have been blamed for the reversion of brightness in pulps during storage so the focus on their behaviour in the Kraft cook has increased dramatically. The hexenuronic acid content of softwood has also been investigated even though pulping hardwood presents greater problems. Gustavsson and Al-Dajani (2000) studied the degradation of hexenuronic acids, assuming the complete formation of hexenuronic acids during the heating stage of the cook. They found that the degradation of hexenuronic acids was promoted by an increase in temperature, hydroxide ion concentration and sodium ion concentration. Increasing the hydrogen sulphide ion concentration, on the other hand, was shown to retard the degradation of hexenuronic acids. However, they only studied the hexenuronic acids content as a concentration in pulp. It is, of course, of great interest to pulp producers to know how to affect the hexenuronic acids content. However, in order to understand the fundamentals behind the formation and degradation of hexenuronic acids, it is also necessary to study the hexenuronic acids content as a function of concentration on the xylan chain. This has been carried out earlier by Bogren (2006).

2.4 Carbohydrate degradation and dissolution kinetics in hardwood Kraft cooking

The history of kinetic modelling of the hardwood Kraft cook is not as long and profound as that of the softwood Kraft cook. Nevertheless, some of the fundamental reactions studied on cotton cellulose are probably directly comparable to the hardwood cook as well as some findings on softwoods, especially where cellulose reactions are concerned.

Giudici and Park (1996) modelled the carbohydrate content of hardwood pulp by considering the total carbohydrate content and the three reactions of peeling, stopping and alkaline hydrolysis, shown in Equations 7a-7h:
\[ C = C_N + C_X \]  

\[ \frac{dC_N}{dt} = k_{nl} C_X - (k_{pt} + k_{nl})C_N \]  

\[ \frac{dC_X}{dt} = k_{nl} C_N - k_{pt} C_X \]  

\[ \frac{dC_{pl}}{dt} = k_{pt} C_N \]  

\[ k_{nl} = [\text{NaOH}]^{\frac{1}{2}} e^{(k_1 - E_{nl})} \]  

\[ k_{pt} = [\text{NaOH}][\text{NaHS}]^{\frac{1}{2}} T e^{(k_1 - E_{pt})} \]  

\[ k_{pt} = [\text{NaOH}]^{\frac{1}{2}} T e^{(k_1 - E_{pt})} \]  

\[ T_n = \left( \frac{1}{417} \right) \]  

\( C \) is the total carbohydrate content, \( C_N \) a fraction known as “native” carbohydrates, \( C_X \) a fraction known as “oxidised” carbohydrates and \( C_D \) the dissolved carbohydrates. The activation energy \( E \) was found to be 220, 68 and 55 kJ/mol for the alkaline hydrolysis, peeling and stopping reactions, respectively. The activation energy for the alkaline hydrolysis is known to be higher than that for the peeling reaction. An activation energy of 220 kJ/mol for the alkaline hydrolysis reaction is, nonetheless, extremely high.

Mirams and Nguyen (1996) divided the carbohydrates into two components, cellulose and hemicelluloses, when they modelled the dissolution of the carbohydrates in a *Eucalyptus globulus* Kraft cook. They fitted the data to two fractions of each component reacting in a parallel manner. The kinetic expressions can be seen in Equation 8:
where $c_i$ is the component (i.e. hemicellulose or cellulose) with $i$ representing the current phase. They found the activation energy for the hemicelluloses dissolution to be 50 and 118 kJ/mol for the first, more rapid, phase and the slower phase, respectively. The activation energy for the corresponding cellulose phases was found to be 125 and 160 kJ/mol, respectively.

Xylan is more common in hardwood, so the amount of hexenuronic acids in hardwood pulps is also higher than in softwood pulps. The reaction kinetics for the hexenuronic formation and degradation have been investigated earlier by Danielsson et al. (2006). They studied the formation of hexenuronic acids from methylglucuronic acids, the degradation of methylglucuronic acids and the degradation of the hexenuronic acids in birch wood. The activation energy for the formation of hexenuronic acids, degradation of methylglucuronic acids and degradation of hexenuronic acids on the xylan chain was found to be 129, 143 and 141 kJ/mol, respectively.

### 3 Experimental

The experiments were conducted using laboratory-screened industrial chips. The hardwoods used were *Eucalyptus urophylla* and *Eucalyptus grandis*; the softwood was Norway spruce (*Picea abies*). The chips were sorted manually to remove knots and bark. Air-dried chips were then pre-treated with steam at a pressure of 2 bar for 10 minutes. Cooking liquor, prepared from technical grade NaOH, Na$_2$S and NaCl, was added at a liquor-to-wood ratio of 50:1 for the softwood experiments and 4:1 for the hardwood experiments. The liquor-to-wood ratio for softwood was chosen to minimize variations in the concentration of the cooking chemicals and the effect of the dissolved wood components (Sjödahl (2004) and Yllner and Enström (1957)). The autoclaves were pressurized with 9 bar nitrogen gas and pre-warmed for 30
minutes in a 90°C polyethylene glycol bath. The pressure was released and the temperature was increased over a period of 60 minutes until the cooking temperature was reached. In the softwood cooks, the concentrations of the cooking chemicals analysed after the 30 minutes of impregnation were fitted into the kinetic models. The hydroxide ion concentration was determined according to SCAN 33:94 and the hydrogen sulphide ion concentration was analyzed according to SCAN 31:94. The kappa number of the pulp was measured according to SCAN 1:00 for all the cooks, and the hexenuronic acid content of the pulp was determined according to a method described by Vuorinen et al. (1996). Analysis of the carbohydrate composition of both the chips and the pulp was performed using High Performance Liquid Chromatography, HPLC, after samples were prepared according to TAPPI 249 cm-85. The pulp viscosity was determined according to SCAN CM 15:99 and the pure cellulose viscosity was calculated from the pulp viscosity times the weight fraction of the cellulose content of the pulp. The lignin content of the chips was determined as “Klason lignin” according to the Tappi method T 222 om-83. The carbohydrate content of the pulp, using the softwood data, was calculated as the percentage of wood based on the monomer results of the carbohydrate analysis according to the expressions in Equation 9a-9c (Meier (1958)):

\[
\begin{align*}
Cellulose &= \text{Glucose} - \frac{1}{3.5} \text{Mannose} \\
Glucomannan &= \text{Mannose} \left(1 + \frac{1}{3.5}\right) + \text{Galactose} \\
Xylan &= \text{Xylose} + \text{Arabinose}
\end{align*}
\]  

The Mathworks Inc. Matlab® 7.0 software with the Optimization toolbox was used for the fitting of the kinetic expressions. The data was fitted to the expression using the function “lsqcurvefit”, which is a non-linear least squares solver.

The multivariate software Umetrics Modde 7.0 was used for the planning and modelling of the eucalyptus experiments.
4 Results and Discussion

4.1 Carbohydrate degradation and dissolution in softwood Kraft cooking (Results presented in Paper I and Paper II)

The degradation and dissolution of carbohydrates during the Kraft cooking process are not only of great importance for the yield of the pulp: they also affect the quality of the pulp. The composition of the pulp and the length of the carbohydrate polymers are crucial to the property of the end product, so it is important that the degradation and dissolution of carbohydrates are controlled during the Kraft cooking process. The results are from experiments using the softwood Norway spruce (*Picea abies*).

Unless stated, the solid lines in all the figures are the fitted kinetic expressions presented later.

4.1.1 The effect of temperature

The dependence of cellulose dissolution on temperature can be seen in Figure 9. The time 0 in the figures below (Figs. 11-22) is the time when the temperature started to increase from 90° C up to the cooking temperature. It shows that there is a shift in the reaction pattern at around 40% on wood where the early, rather steep, trend is followed by a much flatter progress of the dissolution phase.
Figure 9. The decrease in cellulose content at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, an hydroxide ion concentration of 0.51 mol/l and temperatures of 170°C (△), 160°C (□), 150°C (○) and 140°C (▽).

Figure 10 shows the dissolution of xylan: about 50% of the xylan is dissolved in a more rapid phase, followed by a slower dissolution phase.

The dissolution of glucomannan at different temperatures can be seen in Figure 11: almost 80% of the native glucomannan content is dissolved rapidly during the Kraft cooking process.
Figure 11. The decrease in glucomannan content at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, an hydroxide ion concentration of 0.51 mol/l and temperatures of 170°C (Δ), 160°C (○), 150°C (▼) and 140°C (▲). The amount of glucomannan at the beginning of the cook is 20.2% on wood.

Figure 12 shows the cellulose viscosity at different temperatures. The cellulose viscosity is dependent on the temperature since a higher viscosity is preserved when cooking at lower temperatures.

Figure 12. Cellulose viscosity at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, an hydroxide ion concentration of 0.51 mol/l and temperatures of 170°C (Δ), 160°C (○), 150°C (▼) and 140°C (▲).

The degradation of the xylan substituent, hexenuronic acid, at different temperatures is shown in Figure 13. As can be seen, the cooks carried out for long times at the different temperatures result in low contents of hexenuronic acid at a given xylan content.
Figure 13. Hexenuronic acid content at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, a hydroxide ion concentrations of 0.51 mol/l and temperatures of 170°C (△), 160°C (○), 150°C (■) and 140°C (▽).

4.1.2 The effect of the hydroxide ion concentration

The dissolution of cellulose at varying hydroxide ion concentrations can be seen in Figure 14. A higher hydroxide ion concentration results in a more rapid dissolution of cellulose. In the area of investigation the cellulose is mainly degraded by alkaline hydrolysis, followed by secondary peeling. The curvature at the beginning of the cook is the result of the temperature being elevated from 90°C to 170°C in the first 60 minutes.

Figure 14. The decrease in cellulose content at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170°C and hydroxide ion concentrations of 0.89 (△), 0.51 (○), 0.33 (■) and 0.15 (▽) mol/l.
The dissolution of xylan is increased by an increase in hydroxide ion concentration. The xylan dissolution is rapid down to a certain level, depending on the hydroxide ion concentration in the cooking liquor, as can be seen in Figure 15.

![Figure 15](image1.png)

**Figure 15.** The decrease in xylan content at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170ºC and hydroxide ion concentrations of 0.89 (△), 0.51 (□), 0.33 (○) and 0.15 (▽) mol/l.

The degradation of the cellulose polymer increases when the hydroxide ion concentration increases. It is probable that the decrease in cellulose viscosity is mainly dependent on the alkaline hydrolysis of the glucosidic bonds, which is a reaction influenced by the hydroxide ions. The degradation at different hydroxide ion concentrations can be seen in Figure 16.

![Figure 16](image2.png)

**Figure 16.** Cellulose viscosity at a hydrogen sulphide ion concentration of 0.20 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170ºC and hydroxide ion concentrations of 0.89 (△), 0.51 (○), 0.33 (○) and 0.15 (▽) mol/l.
4.1.3 The effect of the hydrogen sulphide ion concentration

The hydrogen sulphide ion concentration is most often excluded as a variable in carbohydrate studies. Figure 17 shows how the hydrogen sulphide ion concentration affects the cellulose content of the pulp. It seems that a higher hydrogen sulphide ion concentration increases the cellulose dissolution but, as the results are scattered, it is difficult to draw definite conclusions from these results. It has been shown earlier by Gustavsson and Al-Dajani (2000) that the cellulose dissolution is somewhat increased by an increased in the hydrogen sulphide ion concentration.

![Figure 17. The decrease in cellulose content at a hydroxide ion concentration of 0.51 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170ºC and hydrogen sulphide ion concentrations of 0.50 (△), 0.30 (○), 0.20 (○) and 0.10 (▽) mol/l.](image)

The effect of the hydrogen sulphide ion concentration on the dissolution of xylan and glucomannan is small, although it seems that an increase in hydrogen sulphide ion concentration increases the dissolution of the hemicelluloses slightly, see Figure 18. The fact that xylan and glucomannan are affected slightly by the hydrogen sulphide ion concentration is a little surprising, even though the same tendencies have been reported earlier by Lémon and Teder (1973) and Lindgren (1997). It is reasonable to believe that the effect is secondary, i.e. the carbohydrates are dissolved dependent on
the dissolution of lignin either as fragments bound to dissolved lignin or as a result of increased accessibility.

Figure 18. The decrease in the total amount of hemicelluloses in the pulp at different hydrogen sulphide ion concentrations. The solid lines in the figure are not fitted kinetic expressions.

The hydrogen sulphide ion concentration does not affect the degradation of hexenuronic acids, as Figure 19 shows. This result is not, however, surprising when the reaction patterns of the hexenuronic acids are considered.

Figure 19. Hexenuronic acid content at a hydroxide ion concentration of 0.51 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170°C and hydrogen sulphide ion concentrations of 0.50 (Δ), 0.30 (○), 0.20 (•) and 0.10 (▽) mol/l.
The relationship between the hydrogen sulphide ion concentration and the cellulose viscosity is shown in Figure 20. The cellulose viscosity is calculated using only the mass of cellulose in the pulp sample. The figure shows that the cellulose viscosity is not influenced by the concentration of hydrogen sulphide ions.

Figure 20. The decrease in cellulose viscosity at a hydroxide ion concentration of 0.51 mol/l, a sodium ion concentration of 1.50 mol/l, a temperature of 170ºC and hydrogen sulphide ion concentrations of 0.50 (△), 0.30 (○), 0.20 (○) and 0.10 (▽) mol/l.

4.1.4 The effect of sodium ion concentration

The ionic strength of industrial cooking liquor is mainly dependent on the sodium ion concentration and its counter-ions. It is the reason why the sodium ion concentration is often used to simulate the effect of the ionic strength in the cooking liquor. The sodium ion concentration of the cooking liquor has earlier been shown to have a significant effect on the rate of delignification (Teder and Olm (1981)).

It is evident from Figure 21 that the cellulose viscosity seems to have no, or only a very small, dependence on the sodium ion concentration. Earlier, Lindgren (1997) found that the degradation of carbohydrates, measured as the carbohydrate viscosity, was accelerated by an increase in sodium ion
concentration. He used the carbohydrate viscosity instead of the cellulose viscosity, however, which means that the total amount of carbohydrates in the pulp was used to calculate the viscosity. Considering the results found by Lindgren (1997) and those of the present study, it could be interpreted as being the composition of the pulp, i.e. the yield of the different carbohydrates, that is affected by the sodium ion concentration and not the degradation of the cellulose chains. It has also been shown by da Silva Perez and van Heiningen (2002) that the amount of hemicelluloses in the pulp sample, up to levels of about 30 %, does not affect the viscosity results, whereas the amount of cellulose in the sample does.

Figure 21. Cellulose viscosity at a hydrogen sulphide ion concentration of 0.20 mol/l, an hydroxide ion concentration of 0.51 mol/l, a temperature of 170°C and a sodium ion concentration of 3.0(△), 2.2(○), 1.5(□) and 0.8(▽) mol/l.

The idea presented above, i.e. that the carbohydrate composition in the pulp actually affects the pulp viscosity measurements, is reinforced by the results found for the dissolution of the carbohydrates at varying sodium ion concentrations. The hemicellulose content has been plotted against the cellulose content in Figure 22. The amount of hemicelluloses in the pulp seems to increase at a given cellulose content when the sodium ion concentration of the cooking liquor is increased. This could be due to the fact that, during Kraft cooking, both glucomannan and xylan are preserved better in the pulp in the form of lignin carbohydrate complexes, and that lignin dissolution is retarded by an increase in sodium ion concentration (Teder and Olm (1981)).
4.2 A kinetic model for carbohydrate degradation and dissolution
(Results presented in Paper I and Paper II)

The data obtained has to be fitted into a kinetic expression in order to facilitate the comparison of results presented earlier and, hopefully, to be able to use the results to simulate the Kraft cooking process in a satisfactory manner. The basis of the kinetic expressions was the findings made by Andersson et al. (2003); it was imperative that the expressions also covered the cooking variables of hydrogen sulphide ion concentration and sodium ion concentration. It was desirable that they not only fit the data well but could also be explained by chemical knowledge of the Kraft cooking process. The expressions used are those given in Equations 10a and 10b:

\[
\frac{dW_p}{dt} = -k_p \left( [OH^-] [HS^-] [Na^+] \right) W_p
\]

\[
k_i = Ae^{-\frac{E_i}{RT}}
\]
where \( w \) is the wood component, i.e. cellulose, glucomannan, xylan, hexenuronic acid or the cellulose viscosity. The data for the three carbohydrate polymers was fitted to expressions consisting of two or three parallel phases: the actual phase is denoted by \( p \) in Equation 10a. Since the data is collected from pulps of kappa number 85 or below, the results in the initial phase of the cook are lacking; the number of phases for the carbohydrate dissolution was limited to two. This was only possible for xylan and cellulose, whereas the glucomannan data had to be fitted with three parallel phases. Only one phase was needed for modelling the cellulose viscosity and the hexenuronic acids concentration on the xylan chain. The constants \( a \), \( b \) and \( c \) are the exponents for the different chemical concentrations. The temperature dependence was modelled with an Arrhenius expression with the activation energy \( E_A \) and the pre-exponential factor \( A \).

4.2.1 The kinetics of the dissolution of cellulose

The dissolution of cellulose was found to be best described in two phases: one initial and one final. The rapid initial phase consisted of 4.2% cellulose on wood with an activation energy of 153 kJ/mol, an hydroxide ion exponent of 1.49 and an sodium ion exponent of 0.58. The exponent of the hydrogen sulphide ion concentration was not found to be significant and the data was very scattered. The same applies to the exponent of the hydrogen sulphide ion concentration in the slower final phase. The final phase was found to consist of 39.8% cellulose on wood with an activation energy for the final phase of 151 kJ/mol together with exponents of 0.83 and 0.38 for the hydroxide ion concentration and the sodium ion concentration, respectively. The final phase has earlier been found to have an activation energy of 150 kJ/mol and 144 kJ/mol by Pu et al. (1991) and Andersson et al. (2003), respectively.

The exponent of the hydroxide ion concentration was found to be larger for the initial phase than the final phase. This might seem odd, especially as the initial phase most certainly consists of peeling reactions that are often claimed to have a lower dependence on the hydroxide ion concentration than
the final phase, which consists of alkaline hydrolysis and is claimed to have a greater dependence on the hydroxide ion concentration. The same differences were expected regarding the activation energy since it has earlier been shown that the activation energy for peeling and alkaline hydrolysis differs significantly (Haas et al. (1967) and Lai and Sarkanen (1967)).

4.2.2 The kinetics of the dissolution of xylan

The activation energy for the dissolution of xylan was found to be 158 and 160 kJ/mol in the initial and final phase, respectively. Earlier studies on the dependence of xylan on temperature have varied significantly. Pu et al. (1991) found the activation energy for the total hemicellulose dissolution to be 35 and 93 kJ/mol for the initial and final phase, respectively. Christensen et al. (1983) studied the dissolution of xylan as one phase system. They found the activation energy to be 167 kJ/mol, but that of cellulose and glucomannan dissolution to be significantly lower.

It was established, as far as the data of the dissolution of xylan at different hydroxide ion concentrations is concerned, that it was impossible to fit the data to the expression used: the amount of xylan reacting as a slower final phase xylan was actually dependent on the hydroxide ion concentration. A new expression had to be introduced that described the amount of xylan reacting in the rapid initial phase and the slower final phase. The expression is shown in Equations 11a and 11b:

\[ X_i = X_t - X_f \]  \hspace{1cm} [11a]

\[ X_f = -4.082 [OH^-] + 6.026 \]  \hspace{1cm} [11b]

where \( X_t \) is the total amount of xylan at the beginning of the cook (in this case 7.6% on wood), \( X_i \) the amount of xylan reacting as initial phase xylan and \( X_f \) the amount of xylan reacting as final phase xylan. The amount of
xylan that reacts in the initial and final phases at different hydroxide ion concentrations can be seen in Figure 23. It is important to remember that the temperature is raised from 90ºC to 170ºC during the first 60 minutes and that the expressions used to estimate the amount of xylan reacting as initial or final phase xylan only work for cooks of constant composition.

![Figure 23. The decrease in xylan content in the initial and final phase at a hydrogen sulphide ion concentration of 0.20 mol/l, sodium ion concentration of 1.50 mol/l, temperature of 170ºC and hydroxide ion concentrations of 0.89 (- - -), 0.51 (- -), 0.33 (· ·) and 0.15 (-) mol/l.](image)

The exponent of the hydroxide ion concentration was found to be 0 for the initial phase and 0.62 for the final phase. This shows that the rate of dissolution at a given hydroxide ion concentration is lower for xylan dissolution than for cellulose dissolution. However, as pointed out earlier, the amount of xylan that reacts as initial or final phase xylan is highly dependent on the hydroxide ion concentration.

The results of the exponent of the hydrogen sulphide ion concentration were not found to be significant when the evaluation test presented in Paper I was used.

The data fitted for the sodium ion concentration was also found to be scattered. The sign of the exponent of the sodium ion concentration was, however, found to be negative for both the initial and final phase, which means that xylan dissolution is retarded by an increased sodium ion
concentration. This, too, has already been seen by Lindgren (1997) and Gustavsson and Al-Dajani (2000).

### 4.2.3 The kinetics of the dissolution of glucomannan

The data for glucomannan dissolution was fitted in three phases where the initial phase was the largest, comprising ¾ of the total amount of glucomannan or 15.5% glucomannan on wood. The activation energy in the initial phase was found to be 70 kJ/mol, the exponent of the hydroxide ion concentration 0 and the exponent of the sodium ion concentration -0.74. The corresponding figures for the intermediate and final phases were 2.6 and 2.1% glucomannan on wood, 121 and 139 kJ/mol, the exponent of the hydroxide ion concentration 0.46 and 0.63 and the exponent of the sodium ion concentration -0.27 and -0.33, respectively.

The dominant reaction in the initial phase of glucomannan dissolution is definitely the peeling reaction, which has been focused on extensively in many papers. The activation energy for the peeling reaction has been found earlier by Haas et al. (1967), Young and Liss (1978) and Wigell et al. (2007) to be just above 100 kJ/mol, which is slightly higher than the result found in this study. However, it is important to remember that most of the data in this study was obtained after the initial phase. This could also been seen from the exponent of the hydroxide ion concentration, which was found to be 0 in this study: Wigell et al. (2007), who focused on the peeling reaction, found the exponent to be 0.36.

Table 1 is a summary of the fitted parameters involved in the dissolution of the different carbohydrates.
Table 1. Initial conditions and fitted parameters.

<table>
<thead>
<tr>
<th></th>
<th>Phase (% ow)</th>
<th>A</th>
<th>Activation energy (kJ/mol)</th>
<th>Hydroxide ion exponent a</th>
<th>Sodium ion exponent c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Initial phase</td>
<td>4.2</td>
<td>1.635E+17</td>
<td>153</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>Final phase</td>
<td>39.8</td>
<td>5.227E+14</td>
<td>151</td>
<td>0.83</td>
</tr>
<tr>
<td>Xylan</td>
<td>Initial phase</td>
<td>X_i = 7.61 - X_t</td>
<td>5.840E+17</td>
<td>158</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Final phase</td>
<td>X_i = -4.082[OH]</td>
<td>3.444E+17</td>
<td>160</td>
<td>0.62</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>Initial phase</td>
<td>15.5</td>
<td>2.829E+7</td>
<td>70</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Intermediate phase</td>
<td>2.6</td>
<td>3.554E+10</td>
<td>121</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>Final phase</td>
<td>2.1</td>
<td>3.346E+14</td>
<td>139</td>
<td>0.63</td>
</tr>
</tbody>
</table>

4.2.4 The kinetics of the cellulose viscosity

The reduction in pulp viscosity is often said to be directly dependent on the alkaline hydrolysis of the cellulose backbone. This study has used only the cellulose content to calculate the viscosity, since da Silva Perez and van Heiningen (2002) showed that it is not the physical properties of hemicelluloses that affect the viscosity of the pulp but rather the content of the hemicelluloses that directly affects the amount of cellulose in the sample measured. The term chosen was the “cellulose viscosity”.

Table 2 shows that the fitted parameters for pulp and cellulose viscosity indicate no large difference except for the effect of the sodium ion concentration, where the exponent for the pulp viscosity is twice as large as that for the cellulose viscosity. The activation energy for the cellulose viscosity was found to be 166 kJ/mol, which was slightly higher than the data found for the alkaline hydrolysis of cotton cellulose presented by Lai and Sarkanen (1967) but, on the other hand, a slightly lower than the 179 kJ/mol presented by Kubes et al. (1983). The activation energy for the cellulose viscosity is higher than the result found for cellulose dissolution in the final phase: this implies that the dissolution of cellulose is not only dependent on the alkaline hydrolysis but also on the secondary peeling, which probably has a lower activation energy than alkaline hydrolysis.
The fact that the exponent for the dependence of the sodium ion concentration for cellulose viscosity is half of that for the pulp viscosity is probably a result of the sodium ion concentration affecting the cellulose dissolution and the hemicellulose dissolution in different directions. This means that alkaline hydrolysis is not affected directly by the sodium ion concentration, which might be the interpretation if the pulp viscosity alone is considered.

Table 2. Initial conditions and fitted parameters for the viscosity data.

<table>
<thead>
<tr>
<th></th>
<th>V0</th>
<th>A</th>
<th>Ea</th>
<th>OH exp.</th>
<th>HS exp.</th>
<th>Na exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>1814</td>
<td>3.317E+17</td>
<td>166 kJ/mol</td>
<td>0.96</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>Viscosity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp viscosity</td>
<td>1422</td>
<td>6.015E+17</td>
<td>169 kJ/mol</td>
<td>0.93</td>
<td>0.05</td>
<td>0.21</td>
</tr>
</tbody>
</table>

4.2.5 The kinetics of the degradation of hexenuronic acid

The assumption was made that all of the methylglucuronic acids reacted instantaneously to form hexenuronic acids when the data for the degradation of hexenuronic acid was fitted. This assumption is probably quite accurate for softwood. The activation energy for the degradation of hexenuronic acids was found to be 120 kJ/mol, which is in accordance with the results found by Gustavsson and Al-Dajani (2000) and Bogren (2006), with 123 and 126 kJ/mol, respectively. It should be noted that the fitted starting value of the hexenuronic acid in wood is, of course, only of importance to the model and is not a real value.

The exponent of the hydroxide ion concentration is 0.91, which is higher than the result of 0.62 found for xylan dissolution. This implies that the hydroxide ion concentration has a greater effect on the rate of degradation of hexenuronic acids than on the rate of dissolution of xylan.

The sodium ion concentration affects, to some extent, the degradation of the hexenuronic acids: this result was seen earlier by Bogren (2006). He explained it with the Donnan effect, which says that the positively-charged
sodium ions screen the negatively-charged fibre wall, thereby promoting a higher concentration of hydroxide ions in the fibre wall. However, the Donnan effect is said not to have any influence at the high sodium ion concentrations of this case. The effect, if present, should probably have been seen for other reactions too (e.g. the cellulose viscosity), but no great influence by the sodium ion concentration could be seen.

A summary of the results of the fitting of the hexenuronic acids data is shown in Table 3.

<table>
<thead>
<tr>
<th>Hexenuronic acid</th>
<th>HexA</th>
<th>A</th>
<th>Ea</th>
<th>QH exp</th>
<th>HS exp</th>
<th>Na exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03</td>
<td>3.360E+12</td>
<td>120 kJ/mol</td>
<td>0.91</td>
<td>0.07</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

4.3 The relationship between hexenuronic acids and xylan in eucalyptus Kraft pulp. (Results presented in Paper III)

It has often been assumed that the content of hexenuronic acid is solely dependent on the amount of xylan in the pulp, i.e. removing the hexenuronic acids automatically involves the removal of xylan, resulting in a substantial loss of yield. A system of three models was fitted with PLS (Partial least squares, projection to latent structure) for the purpose of investigating the relationship between xylan and hexenuronic acids content.

It was found that it is, in fact, possible to produce a pulp with a high carbohydrate yield, i.e. a high xylan yield and comparatively low hexenuronic acids content, as seen in Figure 24.
It is important to remember how xylan reacts during the course of a Kraft cook when discussing the xylan content of pulp. Figure 25 shows how, at lower temperatures, the xylan content decreases slowly. This is in contrast to the xylan content at higher temperatures, where the xylan molecules dissolve rapidly. The xylan yield increases during the cook due to the redeposition of xylan: this phenomenon was seen early on by Yllner and Enström (1957).

Figure 26 shows why it is incorrect to draw the conclusion that a high xylan yield is analogous with a high hexenuronic acids content, and vice versa. It
can be seen that the pulp with the lowest hexenuronic acids content has a high xylan yield.

![Graph showing the correlation between hexenuronic acids and xylan yield.](image)

**Figure 26.** The amount of hexenuronic acids in the pulp correlated with the yield of xylan.

As far as the results of the relationship between the hexenuronic acids and the xylan content are concerned, it could be concluded that the content of hexenuronic acids is not proportional to the amount of xylan in the pulp even though they are connected. Considering the results presented by Danielsson et al. (2006) that show the difference in temperature dependence found in the dissolved xylan and the xylan in the pulp, it is obvious that the system is complex regarding the formation and degradation of hexenuronic acids. A schematic diagram showing the reactions influencing the hexenuronic acids is depicted in Figure 27.

![Diagram showing reactions influencing hexenuronic acids.](image)

**Figure 27.** The reactions influencing the hexenuronic acids in pulp.
The reactions affecting xylan and, indirectly, hexenuronic acids are the alkaline hydrolysis and dissolution of the xylan polymer (1), primary peeling (2), secondary peeling (4) and redeposition of the xylan polymer on the fibre (7). The reactions involving hexenuronic acids directly are the formation of hexenuronic acids from methylglucuronic acid (3) and the degradation of methylglucuronic acid (6) and hexenuronic acid (5).

Taking all these reactions involving hexenuronic acids into account, it is obvious that it is not simply a matter of a low xylan content resulting in a low hexenuronic acids content in the pulp, and vice versa.
5 Industrial aspects

The results obtained from this kinetic study of the Kraft cooking of Norway spruce (*Picea abies*) offer valuable information as to how the different carbohydrates and their side groups are influenced by the cooking conditions. As far as the industrial process is concerned, however, the fate of lignin under different cooking conditions is also very important. An overview of how the cooking conditions affect the composition of the pulp in the diluted systems used in this study is given below. The composition has been calculated from models at the time when the kappa number is estimated at being 30, interpolated from the cooking series.

Figure 28 shows how the carbohydrate composition is affected by the cooking conditions. Should the objective be to vary the carbohydrate composition, then the largest effects can be caused by changing the hydroxide ion concentration and sodium ion concentration.
The ways in which the cellulose viscosity and the hexenuronic acids content are affected by the cooking conditions are shown in Figure 29. The large difference in activation energy can easily be seen from the plot where the temperature has been varied.

Figure 29. The cellulose viscosity(--) and the hexenuronic acids content(- -) at a kappa number of 30 and varying cooking conditions.

Summarizing the above, the cooks at constant composition show that optimum cooking conditions are obtained by keeping the temperature as low as possible, the alkali level at around 0.3 - 0.4 mol/l, the hydrogen sulphide ion concentration as high as possible (if the hexenuronic acids content is not being considering) and, finally, the sodium ion concentrations as low as possible, or at least down to around 1 mol/l.
5 Conclusions

The degradation and dissolution during Kraft cooking of the carbohydrates cellulose, glucomannan and xylan in Norway spruce (*Picea abies*) were studied in this thesis. The results were fitted to kinetic expressions consisting of two or three parallel phases that fitted the data well. The alkaline hydrolysis measured as the pure cellulose viscosity and the amount of hexenuronic acids on the xylan chain was also investigated using kinetic expressions, and showed a good fit. The results were obtained from pulps with kappa numbers of between 5 and 85.

It was found that the dissolution of the different carbohydrates was affected by the temperature, hydroxide ion concentration, hydrogen sulphide ion concentration and sodium ion concentration. The same results were found for the pure cellulose viscosity and the hexenuronic acids content with the exception of the dependence of hydrogen sulphide ion concentration. The most important conclusions to be drawn from the kinetic study of softwood are:

- The concentration of hydroxide ions determined the proportion of xylan reacting as initial or final phase xylan.
- An increase in the hydrogen sulphide ion concentration increased the dissolution of cellulose and hemicelluloses without affecting either the degradation of hexenuronic acids or the cellulose viscosity.
- The sodium ion concentration affected the carbohydrate composition, i.e. the amount of hemicelluloses at a given cellulose yield.
- The sodium ion concentration affected the pulp viscosity twice as much as it affected the pure cellulose viscosity.
The results showed that a high xylan yield in the hardwood pulp was not always synonymous with high hexuronic acids content even if the two are closely connected.
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7 References


Carbohydrate degradation and dissolution during Kraft cooking

Chemical pulp fibres from wood are commonly used in products associated with packaging as well as with printing and writing. The prevalent way of liberating fibres is by subjecting wood chips to Kraft cooking. This process has a history of almost 130 years and should be both well described and well established. However, new products and new applications that use fibres as an important renewable resource make it all the more important that the properties of fibres be controllable. The properties of wood fibres are influenced by their carbohydrate composition which, in turn, is dependent on the cooking conditions used. This thesis studies the degradation and dissolution of the different carbohydrates during Kraft cooking and summarises the results in kinetic expressions.

Industrial wood chips from Norway spruce (Picea abies) were cooked at a high liquor-to-wood ratio in an autoclave digester at varying concentrations of hydroxide ions, hydrogen sulphide ions and sodium ions as well as varying temperatures. The pulps were analysed for carbohydrate composition, kappa number, content of hexenuronic acid and the pure cellulose viscosity, i.e. only the cellulose content in the pulp sample was used for calculating the viscosity. Kraft cooking of Eucalyptus urophylla and Eucalyptus grandis was also studied, using industrial liquor-to-wood ratios, to examine the relationship between hexenuronic acids and the amount of xylan in the pulp samples.

For Kraft cooking of Norway spruce it was found that an increase in the concentration of hydroxide ions increased the rate of dissolution of the carbohydrates and the degradation of the cellulose degree of polymerization (DP). However, measured at a kappa number of 30, it is seen that a low hydroxide ion concentration can lower the carbohydrate yield and the pure cellulose viscosity dramatically. The hydroxide ion concentration not only affects the rate of dissolution but also the amount of xylan that reacts in the slower, final phase. Both cellulose and hemicelluloses were found to be affected by the hydrogen sulphide ion concentration. The dissolution of cellulose and hemicelluloses at varying sodium ion concentrations was found to be affected in different directions. The effect of sodium ion concentration on the DP was found to be dependent on the method of evaluation. The pulp viscosity was found to be affected twice as much by the sodium ion concentration than the pure cellulose viscosity was. For Kraft cooking of hardwood it was found that a high xylan yield not always is synonymous with a high hexenuronic acids content.